

IV.H.17 Heavy Cycloadditions: Reactions of Digallene with Cyclic Polyolefins

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Objectives

- We are interested in investigating the interactions of low-valent Group 13 heavy alkene analogues with a variety of small molecules.
- To investigate uncatalysed, room temperature cyclization reactions of digallene with a variety of cyclic polyolefins.

Technical Barriers

Facile activation of cyclic polyolefins has not been investigated with terphenyl-stabilized digallene prior to this work.

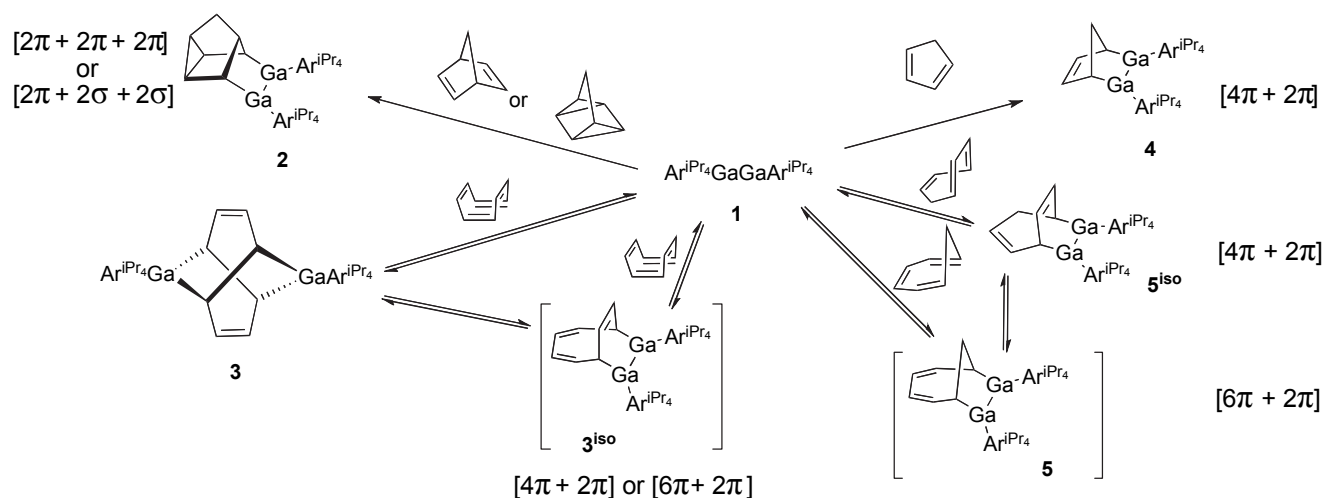
Abstract

The heavier group 13 element alkene analogue, digallene $\text{Ar}^{\text{iPr}_4}\text{GaGaAr}^{\text{iPr}_4}$ (**1**, $\text{Ar}^{\text{iPr}_4} = \text{C}_6\text{H}_3\text{-}2,6\text{-}(\text{C}_6\text{H}_3\text{-}2,6\text{-}$

$\text{iPr}_2)_2$), was shown to react readily in an $[n + 2]$ (where $n = 6, 4, 2+2$) cycloaddition reaction with norbornadiene (NBD), quadricyclane, 1,3,5,7-cyclooctatetraene (COT), 1,3-cyclopentadiene (CpH) and 1,3,5-cycloheptatriene (CHT) to afford the heavier element deltacyclane species $\text{Ar}^{\text{iPr}_4}\text{Ga}(\text{C}_7\text{H}_8)\text{GaAr}^{\text{iPr}_4}$ (**2**), pseudo-inverse sandwich $\text{Ar}^{\text{iPr}_4}\text{Ga}(\text{C}_8\text{H}_8)\text{GaAr}^{\text{iPr}_4}$ (**3**, **3^{iso}**) and polycyclic compounds $\text{Ar}^{\text{iPr}_4}\text{Ga}(\text{C}_5\text{H}_6)\text{GaAr}^{\text{iPr}_4}$ (**4**) and $\text{Ar}^{\text{iPr}_4}\text{Ga}(\text{C}_7\text{H}_8)\text{GaAr}^{\text{iPr}_4}$ (**5**, **5^{iso}**) under ambient conditions. These reactions are facile, and may be contrasted with other all-carbon versions which require transition metal catalysis or forcing conditions (temperature, pressure) or with the corresponding heavier group 14 species $\text{Ar}^{\text{iPr}_4}\text{EEAr}^{\text{iPr}_4}$ ($\text{E} = \text{Ge}, \text{Sn}$) which gave very different product structures. We discuss several mechanistic possibilities including radical and non-radical mediated cyclization pathways. These mechanisms are consistent with the improved energetic accessibility of the lowest unoccupied molecular orbital of the heavier group 13 element multiple bond in comparison to that of a simple alkene or alkyne. We show that the calculated frontier molecular orbitals of $\text{Ar}^{\text{iPr}_4}\text{GaGaAr}^{\text{iPr}_4}$, are of $\pi\text{-}\pi$ symmetry which allows its engagement in a wider range of reactions than that of the usual $\pi\text{-}\pi^*$ frontier orbitals of C-C π -bonds or the $\pi\text{-}n^+$ frontier orbitals of heavier group 14 alkyne analogues.

Progress Report

We have shown that the double bonded digallene, $\text{Ar}^{\text{iPr}_4}\text{GaGaAr}^{\text{iPr}_4}$, behaves as a highly reactive heavy alkene analogue in cyclization reactions with polyolefins including i) the $[4\pi + 2\pi]$ reaction with cyclopentadiene



SCHEME 1. Cycloaddition of various polyolefins with $\text{Ar}^{\text{iPr}_4}\text{GaGaAr}^{\text{iPr}_4}$, **1**.

and cycloheptatriene ii) $[6\pi + 2\pi]$ cyclization reaction with cycloheptatriene and cyclooctatetraene and iii) $[2\pi + 2\sigma + 2\sigma]$ and $[2\pi + 2\pi + 2\pi]$ quadricyclane and norbornadiene respectively to furnish digalladeltacyclane. The higher-order ring structures obtained are only achievable under catalytic conditions in the all-carbon system or with highly electron deficient alkenes. The increased reactivity is attributed to the smaller highest occupied molecular orbital-lowest unoccupied molecular orbital gap and the π - π symmetry of the frontier molecular orbitals of $\text{Ar}^{\text{iPr}^4}\text{GaGaAr}^{\text{iPr}^4}$ which is in sharp contrast to the frontier orbitals of alkenes, alkynes and their heavier group 14 element analogues. The increased electrophilicity and nucleophilicity of these species and their propensity to undergo non-radical cyclization pathways make them closer analogues to the all-carbon system than the heavier group 14 analogues which behave in a manner more consistent with significant diradicaloid character [1].

Future Directions

Singlet carbenes have been shown to react with 2 π equivalents to form stable cyclopropanes [2] and singlet silylenes [3] and germynes [4] have both been shown to undergo preferential $[2 + 1]$ and $[4 + 1]$ cyclizations. We see no evidence for $[n + 1]$ (where $n = 2, 4, 6$) cyclization products, which would arise from the reaction of a $\text{Ar}^{\text{iPr}^4}\text{Ga}$: monomer with an alkene, diene or triene, though a mechanism involving a multi-step reaction of between a cyclic polyolefins and two equivalents of $\text{Ar}^{\text{iPr}^4}\text{Ga}$: monomer remains a possibility. We also highlight that all structures obtained possess two ' $\text{Ar}^{\text{iPr}^4}\text{Ga}$ ' fragments, and compounds **2**, **4**, and **5**^{iso} maintain an intact Ga-Ga bond. We believe this is convincing evidence for the formulation and reactivity of these dimetallene species as heavier group 13 alkene analogues rather than weakly associated monomers. Further investigations regarding the mechanistic details of these cycloaddition reactions are underway.

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